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# The Dielectric Properties of Ferroelectric Bismuth Vanadate, $\text{Bi}_2\text{VO}_{5.5}$ under Pressure

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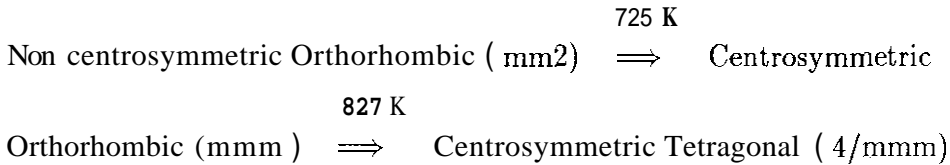
## Abstract

The dielectric properties of single crystals and ceramics of  $\text{Bi}_2\text{VO}_{5.5}$  have been investigated as a function of pressure up to 4 GPa at room temperature. The dielectric constant and the loss are found to decrease with increase in pressure for all the samples under study. However, the rate of decrease of the dielectric constant in the case of partially grain oriented ceramic is higher than that of the single crystal and conventionally synthesised ceramic. The decrease in dielectric constant with increase in pressure is attributed to the decrease in ionic polarisation as a consequence of the decrease in interionic distances.

## 1 Introduction

The dielectric and ferroelectric properties of a large number of crystals belonging to the perovskite family have been investigated under pressure<sup>1</sup>. The most striking effect of pressure on ferroelectric properties, from the thermodynamic point of view, is the shift in the curie temperature ( $T_c$ ). The  $T_c$  decreases with increasing pressure for displacive type of ferroelectrics<sup>2</sup>. For hydrogen bonded crystals in which the ferroelectric-paraelectric transition is understood to be mixed type involving the order-disorder transition of the proton system to which the displacements of the other ions are strongly coupled, the  $T_c$  decreases with increasing pressure. The  $T_c$  increases with increasing pressure in the case of materials in which the ferroelectric-paraelectric transition is believed to be completely order-disorder type. Yet another class of ferroelectric oxides belonging to the family of multilayered interstitial compounds, commonly known as Aurivillius family of oxides with the general formula

$[\text{Bi}_2\text{O}_2]^{2+}[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$  are also interesting from the structural as well as ferroelectric properties view point <sup>3</sup>, where the metal A is in 12 co-ordination (Ca, Sr, Ba etc) and B is in 6 co-ordination (Ti, Nb, Ta etc). Though, the chemical formula appears to be complicated, the structural scheme of these compounds is quite simple. For instance, the  $n = 2$  member consists of alternation of a layer of  $[\text{Bi}_2\text{O}_2]^{2+}$  with two perovskite like layers of oxygen octahedra <sup>4</sup>. Recent investigations into the  $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$  binary system has yielded a novel phase  $\text{Bi}_2\text{VO}_{5.5}$ . This compound has been reported to be ferroelectric at room-temperature <sup>5,6,7</sup>. Structural studies carried out on both polycrystalline and single crystalline materials suggest that it is the vanadium analogue of an  $n = 1$  member of the above mentioned family of oxides <sup>8</sup> and belonging to a non-centrosymmetric polar orthorhombic system (mm2) with lattice parameters  $a = 16.573(4)$ ,  $b = 5.605(1)$  and  $c = 15.284(3)$  Å. We have been investigating the dielectric, pyroelectric and ferroelectric properties of ceramics as well as single crystals of  $\text{Bi}_2\text{VO}_{5.5}$  as a function of temperature <sup>9</sup>. X-ray powder diffraction studies carried out, as a function of temperature, indicate that bismuth vanadate undergoes two major phase transitions, of the kind mentioned below, at 725K and 827K <sup>10</sup>:



We thought that it is worth examining the dielectric properties of  $\text{Bi}_2\text{VO}_{5.5}$  as a function of pressure in the light of the aforesaid phase transitions, since applying pressure is a more efficient way to alter the inter-atomic distances and also to induce other phase transitions that are not observed at atmospheric pressure. Though, uniaxial pressure studies will be more interesting particularly on the layered compounds, the present studies are made with quasi-hydrostatic pressure, since this allows much higher pressure to be applied without destroying the crystals. We report in this paper, the preliminary results obtained on the studies concerning the effect of quasi-hydrostatic pressure on the dielectric properties of  $\text{Bi}_2\text{VO}_{5.5}$  ceramics and single crystals at room temperature (300 K).

## 2 Experimental

Polycrystalline powders of required  $\text{Bi}_2\text{VO}_{5.5}$  were prepared by heating a stoichiometric mixture of  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  initially upto about 775 K and then at 1070 K for about 24 hours with intermediate grinding steps. The powders were compacted and subsequently sintered at 1070 K for about 24 hours. The density of the sintered disc is  $7.30 \text{ gm/cm}^3$ . Ceramics with partial grain orientation were prepared by quenching the melts of prereacted  $\text{Bi}_2\text{VO}_{5.5}$ . The ceramics were annealed at 1070 K for about 8 hours, before carrying out any physical property studies. The density of these ceramics is  $7.50 \text{ gm/cm}^3$ .

The single crystals employed for the present studies were grown by slow cooling technique. The growth was carried out using a muffle furnace associated with a programmable temperature controller. The prereacted powder of  $\text{Bi}_2\text{VO}_{5.5}$  was packed into a platinum crucible of capacity 100 cc and heated to about 1400 K at the rate of 100 K/hr. It was soaked at this temperature for about 6 hours and cooled at a programmable rate of 5 K/hr down to 900 K. Subsequently it was cooled at the rate of 20 K/hr to 600 K and then the furnace was switched off. The temperature profile of the furnace is shown in Fig. 1. The crystallised melt was found to contain fine shiny platelets embedded in it. The crystals separated mechanically (4mm x 4mm x 0.5mm) were greyish black with layered habit. The single crystalline nature of the grown crystals was confirmed by the X-ray diffraction studies using CAD4 automatic four circle diffractometer ( $\text{MoK}\alpha$  radiation).

The dielectric constant and the loss measurements were carried out at 100kHz using Keithley LCZ meter (model 3330) as a function of pressure using a pair of tungsten-carbide opposed anvils with 12.5 dia anvil face.  $1.5 \times 1.5 \text{ mm}^2$  face and 0.2 mm thick sample was set in a 0.2 mm thick metal gasket (5mm i.d.) with talc and epoxy mixture such that the sample surface was fully exposed on both sides. After allowing the epoxy to set, talc- epoxy disc with the sample was separated from the metal gasket. A pyrophyllite gasket (5 mm i.d. ; 12.5mm o.d. and 0.42 mm thick) was stuck on the anvil along with a 0.28mm thick talc disc inside it, which formed the lower gasket. This gasket contains a copper lead and a bismuth sample along with two leads for in-situ pressure calibration. The talc-epoxy disc with the sample was placed on top of the talc disc in the lower gasket. Another pyrophyllite gasket with the same dimension and also containing a 0.28 mm thick talc disc at the centre

along with a copper lead was placed on top of the lower gasket such that the sample was sandwiched between the copper leads. Aluminium foils cut exactly to the size of the samples were placed between the copper leads and the sample on both sides.

### 3 Results and discussion

The X-ray powder diffraction pattern obtained for the powdered sample heated at 1070 K confirms the formation of the required  $\text{Bi}_2\text{VO}_{5.5}$  phase (Fig. 2a). The X-ray diffraction pattern recorded for the ceramic obtained by quenching the melt suggests that it is polycrystalline (Fig. 2b). However, the intensities of the (001) reflections ( *Viz.* (002) and (006) ) are higher than those of the ceramics obtained by conventional solid state reaction route. It implies that a significant number of grains

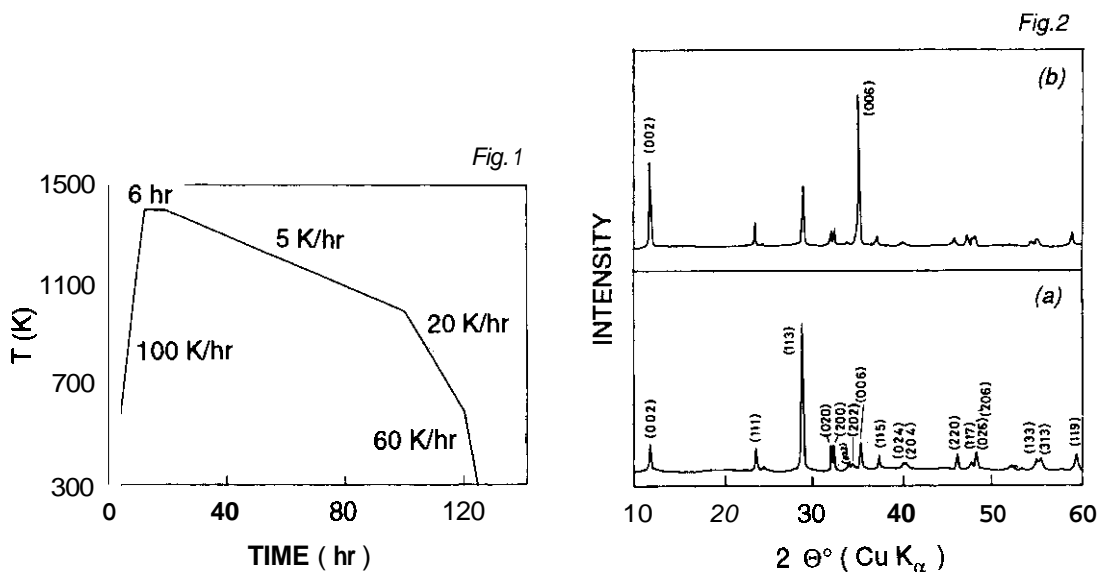


Figure 1: The temperature profile employed to grow single crystals of bismuth vanadate.

Figure 2: X-ray diffraction patterns for the (a) conventionally fired ceramic and (b) ceramic obtained by melt-quenching,

of the ceramics obtained by quenching the melt is oriented along the *c*- direction. The degree of the grain orientation is determined based on the X-ray orientation method

proposed by Lotgering<sup>11</sup>. It is found that 55% of the grains are c-oriented,

The scanning electron micrographs of the ceramics obtained by the conventional solid state reaction route and by quenching the melts are shown in Fig. 3a and b respectively. A rectangular bar shaped grain morphology is found with the ceramic prepared by melt-quenching technique. The average grain size as-determined by the line intercept method is about  $100 \mu\text{m} \times 35 \mu\text{m}$ . The growth rate of the individual grains in the plane normal to the pressing direction appears to be high.

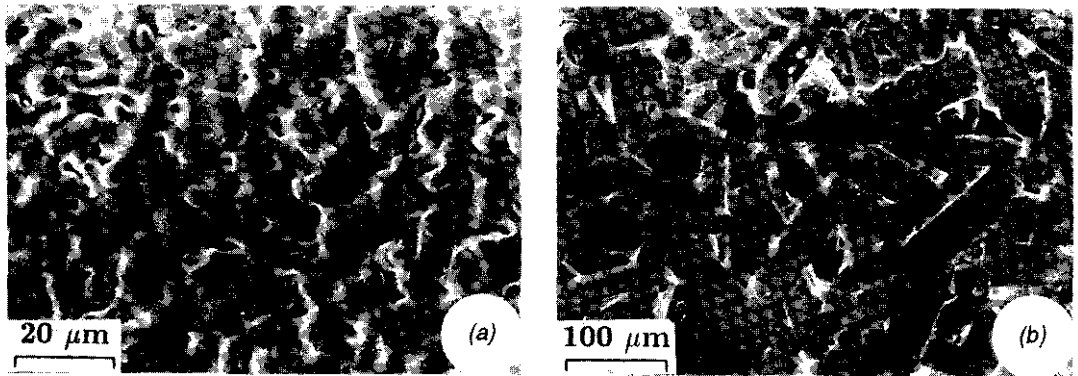


Figure 3: Scanning electron micrographs of unetched (a) conventionally fired ceramic and (b) ceramic obtained by melt-quenching.

Fig. 4 shows the photomicrograph of the grown crystals. The single crystal X-ray diffraction studies indicate that the grown crystals are single crystalline (Fig.5) with unit cell parameters  $a = 16.573(4)$ ,  $b = 5.605(1)$  and  $c = 15.284(3) \text{ \AA}$  and the large faces of the platelets are parallel to the crystallographic plane (001). The present data is consistent with that of Abraham *et al*<sup>12</sup>.

The capacitance and the dielectric loss ( $\tan\delta$ ) measurements at 100 kHz have been carried out on conventionally sintered ceramic, partially grain-oriented ceramic and single crystals (along c-axis) as a function of pressure at room temperature. The dielectric constants have been evaluated by making correction for stray capacitance introduced by the leads etc. Fig. 6 shows the variation of the dielectric constants for the single crystal, conventionally prepared ceramic and partially grain-oriented ceramic as a function of pressure. The dielectric data has been recorded while reloading

the samples. The dielectric constants obtained for all these samples at atmospheric

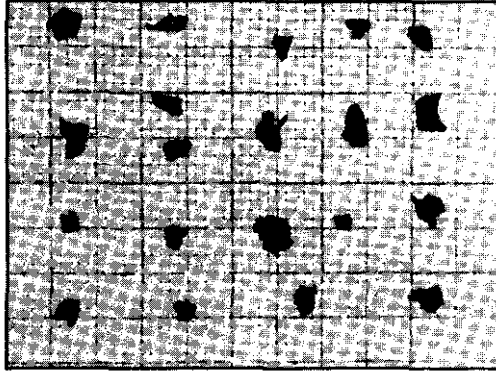


Figure 4: Photograph of grown single crystals of  $\text{Bi}_2\text{VO}_{5.5}$



Figure 5: Oscillation photograph of the grown crystals

pressure are in agreement with those of the values obtained by extrapolating the curves (dotted curves) on to the Y-axis. The dielectric constant in all the three cases decreases with increasing pressure. However, the dispersion of the dielectric constant with pressure in the case of the partially grain-oriented ceramic is higher. The dielectric constant of the partially grain-oriented ceramic is higher up to the pressure of about 1 GPa than that of the conventionally prepared ceramic and single crystal. The dielectric loss ( $\tan \delta$ ) also decreases with increasing pressure in all the cases (Fig.7). No sudden changes either in  $\epsilon_r$  or  $\tan \delta$  have been noticed in the range of pressures under study, indicating that the pressures employed in the

present studies are not adequate to induce any phase transitions. It is known that the dielectric constant can be written in terms of the individual polarizabilities of the ions. Since, the present dielectric constant measurements have been carried out at 100 kHz, the electronic polarizability contribution to the observed dielectric constant is less significant. Therefore, the only significant contribution could be from the ionic polarizability. With increasing pressure the ions in the lattice get closer and as a consequence the elastic restoring forces increase, Hence, ionic polarizability

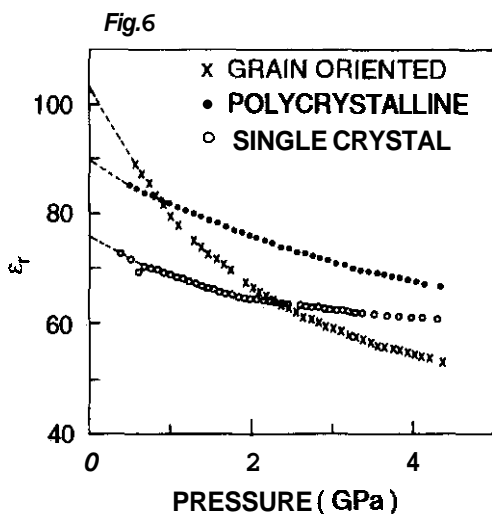


Figure 6: The variation of dielectric constant with pressure for the ceramics and the single crystals (c-axis).

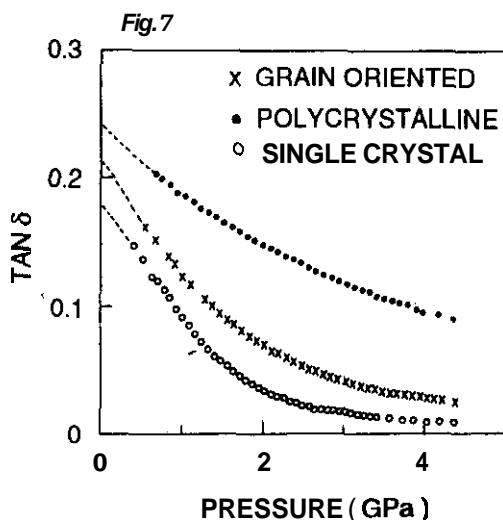


Figure 7: The variation of the dielectric loss ( $\tan \delta$ ) with pressure for the ceramics and the single crystals (c-axis).

which arises due to the ionic displacements and the resulting displacement of the electronic charge distributions can be expected to decrease. Consequently the dielectric constant decreases with increasing pressure. At macroscopic level the decrease in dielectric constant with increasing pressure may also be attributed to the decrease in an orthorhombic distortion ( $b/a$  ratio).

## References

1. G.A. Samara, *Advances in high pressure research*, ed. R.S. Bradley. Vol.3, 1969.
2. G.A. Samara, *Phys. Rev.*, **151**, 378, (1966).
3. B. Aurivillius, *Arkiv Kemi*, **1**, 499, 463, (1949).
4. B. Aurivillius, *Arkiv Kemi*, **2**, 519, (1950).
5. V.N. Borisov, Y.M. Poplavko, P.B. Avakyan and V.G. Osipyan, *Sov. Phys.: Solid State*, **30**, 904, (1988).
6. A.A. Bush and Yu.N. Venevstev, *Russ. J. Inorg. Chem.*, **31**, 769, (1986).
7. V.G. Osipyan, L.M. Savchenko, V.L. Elbakyan and P.B. Avakyan, *Inorganic Materials*, **23(3)**, 467, (1987).
8. K.B.R. Varma, G.N. Subbanna, T.N. Guru Row and C.N.R. Rao, *J. Mater. Res.*, **5(11)**, 2718, (1990).
9. K.V.R. Prasad and K.B.R. Varma, *Mat. Chem. and Phys.*, 38,406, (1994).
10. K.V.R. Prasad and K.B.R. Varma, *J. Mater. Sci.*, (to be published).
11. F.K. Lotgering, *J. Inorg. Nucl. Chem.*, **9**, 113, (1959).
12. F. Abraham, M.F. Debreuille-Gresse, G. Mairesse and G. Nowogrocki, *Solid State Ion.*, **28-30**, 529, (1988).